SYNOPSIS

Name of the candidate	:	Sontakke Sharad Mahadeo
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Research Supervisor	:	Prof. Jayant M. Modak, Department of Chemical Engineering, Indian Institute of Science, Bangalore.

Photocatalysis is an advanced oxidation process, which has shown to possess an enhanced capability to remove a wide range of contaminants. It involves the use of a semiconductor photocatalyst and a photon source. Photocatalysis has several advantages such as mild reaction conditions like ambient temperature and pressure, good control over the reaction and faster reaction kinetics. Semiconductor photocatalysts such as TiO_2, ZnO, Fe_2O_3, CdS, ZnS, etc. absorbs light of energy greater than or equal to its band gap and the electron in the valence band gets excited to conduction band leaving behind the hole in valence band. These charge carrier pair results in the formation of various reactive oxygen species such as hydroxyl and superoxide radicals which results in the degradation of chemical contaminants and inactivation of microorganisms.

TiO_2 is the most widely used catalyst in photocatalytic studies because of its high photocatalytic activity, non-toxicity and wide availability. Anatase phase TiO_2 has been reported to possess higher photocatalytic activity than the rutile phase. Although there are several methods to synthesize TiO_2, solution combustion synthesis is a single step process to produce pure anatase phase TiO_2. The catalyst produced by this method has been shown to be superior to the commercially available Degussa P-25 catalyst for the degradation of various chemical contaminants. The present investigation focuses on the use of combustion synthesized catalyst for the inactivation of microorganisms. The photocatalytic activity was compared with commercial Degussa P-25 catalyst.

The various aspects of photocatalytic inactivation reactions studied in this dissertation are: i) photocatalytic inactivation of microorganisms in presence of UV light, ii) effect of various parameters on the inactivation, iii) photocatalytic inactivation in presence of visible light, iv) use of immobilized catalyst for the photocatalytic inactivation, v) understanding of mechanism and kinetics of inactivation.

Combustion synthesized TiO_2 (CS-TiO_2), combustion synthesized 1% Ag substituted TiO_2 (Ag/TiO_2 (Sub)) and 1% Ag impregnated CS-TiO_2 (Ag/TiO_2 (Imp)) were used as photocatalysts. The catalysts were characterized by powder XRD, TEM, BET surface area, UV-Vis spectroscopy, TGA and photoluminescence spectroscopy. The photocatalytic inactivation experiments were carried out using *E. coli* (K-12 MG 1655), a bacterial strain and *P. pastoris* (X-33), a yeast strain, as model microorganisms.

The results demonstrate higher photocatalytic activity of all the combustion synthesized catalysts than commercial Degussa P-25 catalyst. The optimum catalyst concentration was 0.25 g/L and the maximum inactivation was observed in the presence of Ag/TiO_2 (Imp) catalyst. Rapid and complete inactivation of the microorganisms was observed at lower initial cell concentrations. A reduced photocatalytic inactivation was observed in presence of various anions (HCO_3^-,

SO_4^{2-}, Cl^- and NO_3^-) and cations (Na^+, K^+, Ca^{2+} and Mg^{2+}). Even a small addition of H_2O_2 was observed to improve the photocatalytic inactivation. At higher dosage of H_2O_2, a 2 min exposure was sufficient to result in a complete inactivation. Changing the initial pH of the solution was observed to have no significant effect on the photocatalytic inactivation.

All the combustion synthesized catalysts showed higher activity as compared to those obtained with commercial Degussa P-25 TiO_2 in presence of visible light. The higher photocatalytic activity of combustion synthesized TiO_2 can be attributed to the lesser crystallite size, higher surface area, large amount of hydroxyl groups and decreased band-gap energy of the catalyst.

The present study demonstrates the potential use of catalyst immobilized thin films for the photocatalytic inactivation of *E. coli* in the presence of UV light. The CS-TiO_2 catalyst was immobilized on glass substrate by LbL deposition technique. The performance of immobilized CS-TiO_2 was compared to commercial Degussa Aeroxide TiO_2 P-25 (Aeroxide) catalyst. The effect of various operating parameters like catalyst loading, surface area and number of bilayers on inactivation has been investigated. It was observed that increasing the number of bilayers and the concentration did not influence the inactivation but increased surface area led to an increase in inactivation. It was observed that the catalyst immobilized on glass slides can be used for repeated experimental cycles with the same efficiency. It was observed that the inactivation process can be studied in continuous mode by using catalyst immobilized on glass beads.

The work also focused attention towards understanding the microorganism inactivation mechanism and kinetic aspects. Various microscopy techniques such as optical microscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to study the inactivation mechanism. From the images obtained, it was suggested that the inactivation is caused due to rupture of cell wall. The mechanism was also examined by carrying out degradation experiments on cell component such as protein and media component such as dextrose. UV alone was

observed to degrade protein and the presence of catalyst showed no additional effect. On the other hand, dextrose does not respond to photocatalytic degradation even at a lower concentration. The photocatalytic degradation of Orange G dye was reduced by addition of dextrose sugar or protein which shows a possibility of competitive degradation.

The kinetics of inactivation was studied by various models available in literature such as the power-law model, Chick-Watson model, modified Hom model, GInaFIT tool and a Langmuir-Hinshelwood type model. It was observed that power-law based kinetic model showed good agreement with the experimental data. A mechanistic Langmuir-Hinshelwood type model was also observed to model the inactivation reactions with certain assumptions.